

Glass Fiber/Carbon Nanotubes/Epoxy Three-Component Composites as Radar Absorbing Materials

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The use of micro or nano-fillers to optimize the properties of epoxy resins has become a common practice. The Carbon nanotubes (CNT) are considered excellent fillers because of their strength, stiffness, thermal conductivity, electrical capacity, and thermal stability, along with large electromagnetic wave absorption capability in the microwave range. In this work, electromagnetic absorption properties and dynamic-mechanical response obtained with the incorporation of CNT into glass fiber/epoxy composites have been studied. A novel procedure to disperse and deposit CNT onto glass fiber fabrics has been developed to reach high overall content of CNT in the composite (4.15 wt%). Storage modulus increased with the incorporation of CNT, especially when they had also been incorporated into the epoxy, and for higher frequency (3 Hz). The response of the composites to electromagnetic radiation has shown an increasing trend for higher CNT content (up to 2 wt%), reaching an excellent attenuation value of up to -18.3 dB (98.5% of absorption). *POLYM. COMPOS.*, 37:2277–2284, 2016. © 2015 Society of Plastics Engineers

INTRODUCTION

The use of polymeric composites as structural and multifunctional material in areas such as aerospace has been largely studied by the research community. This is mainly because of characteristics which usually include low density, good mechanical properties, high dimensional, and thermal stability, but also special less-common features like electromagnetic absorption [1].

Glass fiber (GF) composites have been used in structures that demand transparency in the microwave frequency range, for example, in antenna systems for radar data transmission and in aircraft radomes. These fibers do not affect the radiation diagram of the antenna and do not interfere in the transmission–reception of the radar. The transparency characteristic in the case of radar data transmission is a consequence of the low dielectric loss of the GF. However, these composites can behave as microwave absorbers when combined with materials of high dielectric and/or magnetic loss (sometimes called active centers or dielectric absorbers) and, because of that, they may also be used as radar absorbing materials in the microwave frequency range, for example between 2 and 18 GHz [2].

Radar absorbing materials (RAM), also called electromagnetic radiation absorbing materials, are very important for civil and military applications due to their wave-matter interaction. Polymer composites with glass fibers and carbon fibers have been studied aiming their application in this field [2].

In addition, the use of nanoparticles, or more specifically carbon nanotubes (CNT), as active centers to promote microwave absorption in epoxy resin (EP)/GF composites has been reported [3–6]. CNT have like high electrical conductivity, aspect ratio, and mechanical strength, and they are an interesting option for producing multifunction structural composite materials with high electromagnetic shielding performance [7].

CNT have been applied as active centers in EP/GF composites manufactured by resin impregnation with up to 5 wt% of CNT [4]. An increase in electromagnetic shielding efficiency as a function of the CNT content and the thickness of the composite was reported. The measured efficiency in 10-mm thick samples with 5 wt% of CNT reached approximately -20 dB (99% absorption) in

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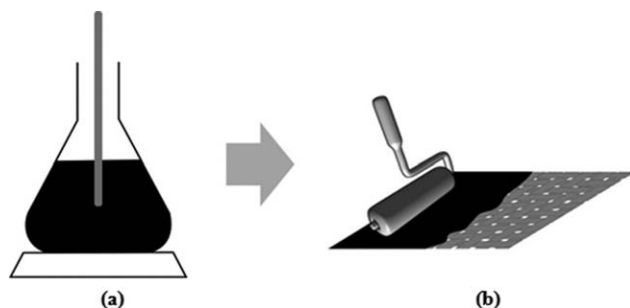


FIG. 1. Preparation of the fibrous reinforcement for RTM: (a) sonication of CNT/acetone suspension, and (b) deposition of the suspension onto the glass fabric.

the frequency range of 0.3–1.0 GHz. In general, sonication and three-roll milling are commonly used techniques to disperse CNT in a polymer resin [8].

In the RAM area, the major goal is to increase microwave attenuation. The challenge there is to find the most adequate combination of parameters like RAM thickness, concentration of the active center, and manufacturing technique. Different structures have been used as RAM, including sandwich structures in which nanocomposites/foams are the core. In this case, even though the active centers still play a significant role in favoring impedance matching (of the constituents), the structure of the foam itself promotes radiation scattering [5, 9]. PVC (polyvinyl chloride) and PMI (polymethacrylimide) are among the most common foam materials for this aim [6, 10], and the final structure may reach a thickness of up to 22 mm. Such a thickness might not be desirable for some applications related to electromagnetic interference, which would benefit from thinner specimens. Overall, the challenge when designing microwave absorbers is the production of a thin and light RAM.

This work describes a novel route for the dispersion and deposition of CNT on glass-fiber fabrics. The route was developed aiming to allow for a very high CNT content in composites produced by resin transfer molding (RTM), and to produce thin materials with microwave attenuation properties in the frequency range of 8.2–12.4 GHz based on the use of CNT as microwave absorbing centers.

EXPERIMENTAL

Materials

The materials used in this work were: epoxy resin LY1316 and hardener HY1208 supplied by Huntsman; two degassing agents (A500 and A560) supplied by BYK; acetone (99.98% purity of NeoN LT) used as solvent for dispersion; multiwalled carbon nanotubes (produced by CVD) from Chegdu Organic Chemicals (outer diameter: 5–30 nm, length: 1–30 μm , 85% purity); plain weave E-glass fiber fabrics from Fibertex (aerial weight: 300 g/m²).

Dispersion and Deposition of the CNT

Some CNT were dispersed in the epoxy resin used to infiltrate the GF reinforcement in the resin transfer molding. For that, 0.25 wt% (relative to the resin) of CNT was suspended in acetone using a tip sonicator (model VCX 750 from Sonics/Vibracell) for 30 min at 165 W (22% amplitude). Then, the epoxy was added to the suspension followed by dispersion for 40 min at 225 W (30% amplitude), with simultaneous magnetic stirring. After that, the solvent was removed by heating (at 60°C) with simultaneous magnetic stirring under vacuum for 1.5 h. Finally, the degassing agents and the curing agent were added, followed by mechanical stirring for 5 min.

Some CNT were also deposited directly onto the GF fabric surface using a process similar to conventional painting. For that, a pre-determined amount of CNT (1, 2, or 4 wt% in relation to the fiber) was dispersed in acetone for sonication (220 W for 40 min). After that, a small amount of resin, about 3 wt% (in relation to composite), was added and the mixture was again sonicated (220 W for 40 min). The CNT/acetone suspension was then deposited with the aid of a roll on the GF fabric surface, as shown in Fig. 1. The wet reinforcement was subsequently dried at 80°C for 2 h in air-circulating oven.

RTM Process

Three-component (EP/GF/CNT) composites were manufactured using the RTM process with radial infiltration, producing flat plates with dimensions of 300 mm \times 300 mm \times 2 mm. The samples were subsequently cured (24 h at room temperature) and post-cured (3 h at 80°C). The composites were produced with variable amounts of CNT (Table 1), keeping the GF volume fraction constant (ca. 30%).

The use of a small amount of epoxy in the CNT/acetone suspension was necessary to make the CNT/acetone suspension adhere to the fabric surface. However, even this small amount of epoxy (without hardener) may fill the spaces between the warp and weft bundles of the

TABLE 1. Formulation of the two-component and three-component composites.

Composites	CNT content in the resin (wt% of resin)	CNT content on the GF (wt% of fiber)	Overall CNT content (wt% of the composite)
EP0/GF0	—	—	—
EP25/GF0	0.25	—	0.15
EP0/GF1	—	1.0	1.00
EP25/GF1	0.25	1.0	1.15
EP0/GF2	—	2.0	2.00
EP25/GF2	0.25	2.0	2.15
EP0/GF2-WE	—	2.0	2.00
EP0/GF4	—	4.0	4.00
EP25/GF4	0.25	4.0	4.15

WE = without adding epoxy to the CNT/acetone suspension.

fabric during their coating and also make the coated fibers less prone to infiltration. Considering that these two factors could interfere with microwave attenuation performance of the composite, one composite called EP0/GF2 was manufactured without adding epoxy to the CNT/acetone suspension for comparison.

Characterization of the Composites

The produced plates were inspected using an acoustic inspection microscope (IM-Scan, Matec Ultrasonics Inspection Software) operating in C-scan mode. The plates were immersed in water and the scan was performed using a 10 MHz focus transducer searching for defects (such as resin rich regions, voids, and dry areas). The total attenuation (dB) transmitted through the thickness of each specimen is given by the MUIS32 software, which converts the received signal into images.

SEM micrographs of the composites were taken using a Jeol model 6060 scanning electron microscope, operating at 10 keV. Comparative analysis of the dynamic mechanical properties of the three-component composites (sample dimensions: $35 \times 15 \times 2 \text{ mm}^3$) was performed using a Dynamic Mechanical Analyzer-2980 TA Instruments, under single cantilever mode, from room temperature to 200°C , using 1 Hz and 3 Hz frequency.

The NRL (Naval Research Laboratories) arch technique was used to perform the electromagnetic characterization by means of reflectivity measurements. This set-up is located at the Laboratory for Electromagnetic Characterization of the Materials Division at IAE (Institute of Aeronautics and Space, Brazil). The arch consists of a wooden structure that allows setting a pair of antennas on a variety of angles. The horn antenna assembly can be moved along this arch. The sample (200 mm square plate) is positioned on a small base at the center of the arch curvature. The arch structure is designed to keep the horn pointing to the center of the specimen under testing. The transmitter and the receiver antennas can be close to each other as long as an absorbing material is positioned between them, to reduce interference between the horns, as illustrated in Dias et al. [11]. The reflectivity measurements were performed in the 8.2–12.4 GHz frequency range, at room temperature. An aluminum metal plate was used as reference sample (100% reflector). An Anritsu spectrum analyzer, model MS 2668C (9 kHz to 40 GHz), was coupled to the system. Six of the tri-component samples were selected for this test since two of them did not achieve the required dimensions for testing.

RESULTS AND DISCUSSION

Dynamic Mechanical Analysis

The storage modulus (E') and $\tan \delta$ of the two-component composites produced without CNT in the resin are shown in Fig. 2. The values of E' for composites tested at 1 Hz were all smaller than those tested at 3 Hz,

as the increase in loading frequency reduces the relaxation time of the polymer chains, increasing E' .

In addition, the E' and $\tan \delta$ values showed a significant increase with the amount of CNT on the fabric surface, except for the composite with 4% of CNT. The significant drop in E' is related to energy dissipation by means of the cooperative movement of polymer chains. This drop allows estimation of the glass transition temperature (T_g), which was between 90 and 110°C for the various composites. This behavior is consistent with that observed by Zhou et al. [12]. In addition, it is possible to predict changes in toughness of the composites by observing the widening of the $\tan \delta$ curves [12] and the increase in peak intensity.

The variation in the E' curves for 3 Hz frequency was more noticeable, and the E' values increased with the increase in CNT content for 1 and 2%. After that, a critical concentration point (4% CNT) was reached where the CNT did not disperse as well, decreasing E' . In an analogous way, a system with the same content of filler should present higher E' when a more efficient dispersion is achieved as, in this case, there is a limited number of aggregates of smaller dimensions, resulting in an increased number of minicapacitors and a shorter distance among them insures higher capacitance and, hence, higher E' [13].

The storage modulus (E') and the $\tan \delta$ of the three-component composite are shown in Fig. 3, and the same overall behavior is shown. Comparing the E' values obtained at different frequencies (Table 2), no clear trend was observed, even though there may be an increase in E' values as a function of the CNT content, especially for higher frequency. There are many factors that influence the mechanical properties of composites reinforced with CNT, such as resin/CNT interaction, CNT agglomeration, and CNT structural parameters (such as aspect ratio, diameter, and number of walls) [14]. Considering that the CNT are mostly deposited on the surface of the GF fabric, a great improvement in E' cannot be expected since the overall area for stress transfer in the CNT/resin interface is not expressive. In fact, CNT in the resin slightly increased the storage modulus, and the EP25/GF4 composite at 3 Hz frequency showed greater interaction with the dispersed CNT. Thus, the increase in storage module suggests an improvement in CNT dispersion in the composite. The SEM micrographs of the fabric make it clear that the CNT agglomerates produced by roll-deposition behave as a type of coating (Fig. 4).

The T_g values at different frequencies (1 and 3 Hz) (Table 3) or for composites with distinct CNT content did not vary significantly. In theory, there may be a correlation between the loss factor of the electromagnetic radiation and the loss coefficient of the material. This physical entity represents electric losses in the material, which is mainly correlated to two different contributions: electrical conductivity and a potential relaxation phenomenon [13]. Observing the various samples in Table 3, the composites with 2 wt% display slightly higher T_g .

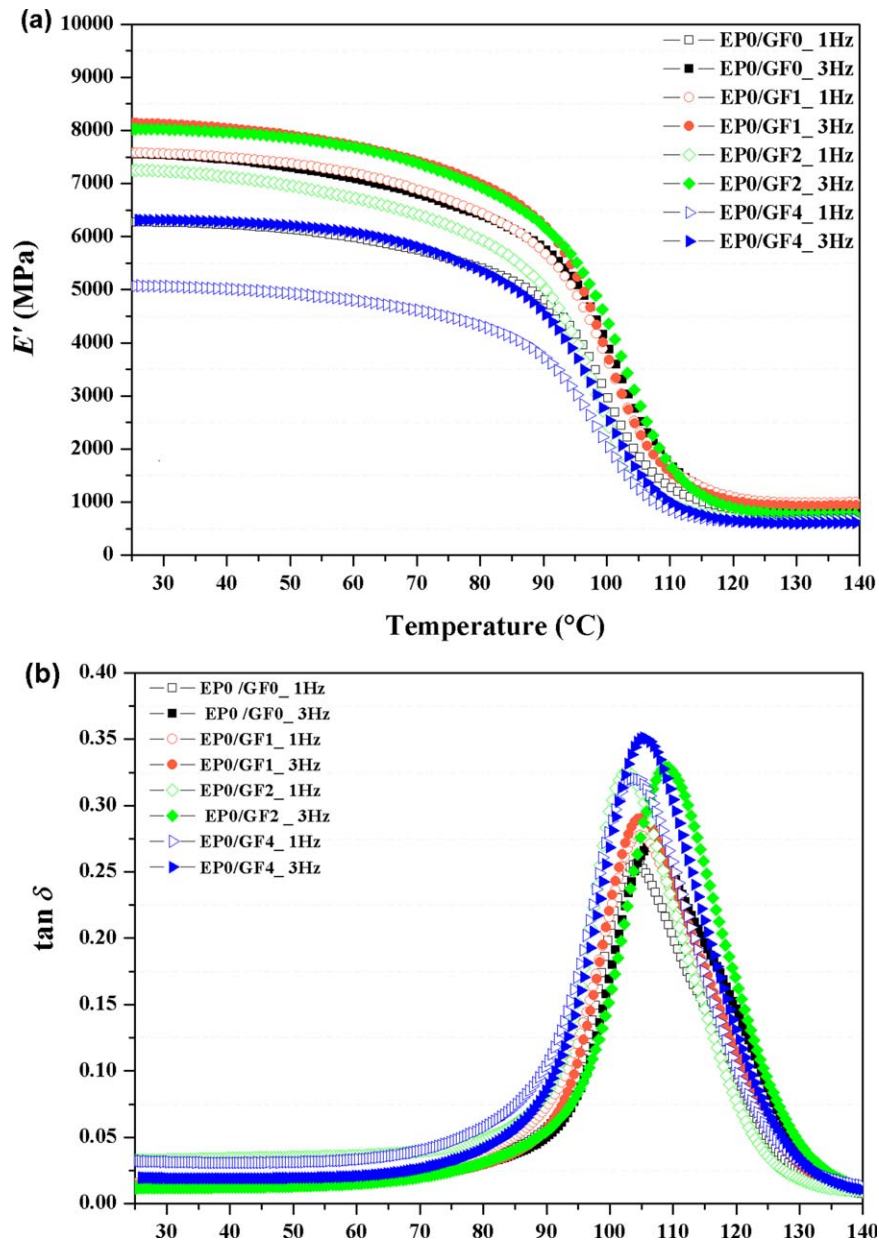


FIG. 2. E' (a) and $\tan \delta$ (b) curves of the composites with CNT deposited on the GF fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ultrasonic Inspection

Figure 5 shows C-scan images of a quarter of each of the produced composite plates. The software *lview* assigns a color scale related to wave attenuation, allowing to analyze impregnation of the GF reinforcement by the resin. The black areas are the perimeter of the molded plate, which does not have glass reinforcement. Dark color is also seen at the geometric center of the mold and refers to a hole which was made in the fibrous reinforcement to promote a more even impregnation of the fiber following radial injection of the resin with CNT.

The best quality areas are shown in green (8 dB attenuation), which is mostly mixed with a blue color (14 dB attenuation). In general, it may be seen that impregnation was not very homogeneous and this is a consequence of the irregular infiltration of the fabric especially due to the thick CNT coating on the surface. It also appears that impregnation is worsen (i.e., the green color becomes scarcer) for higher content of CNT deposited on the fabric.

Reflectivity Analysis

The attenuation response of the various samples in the microwave radiation frequency range (8.2–12.4 GHz) is

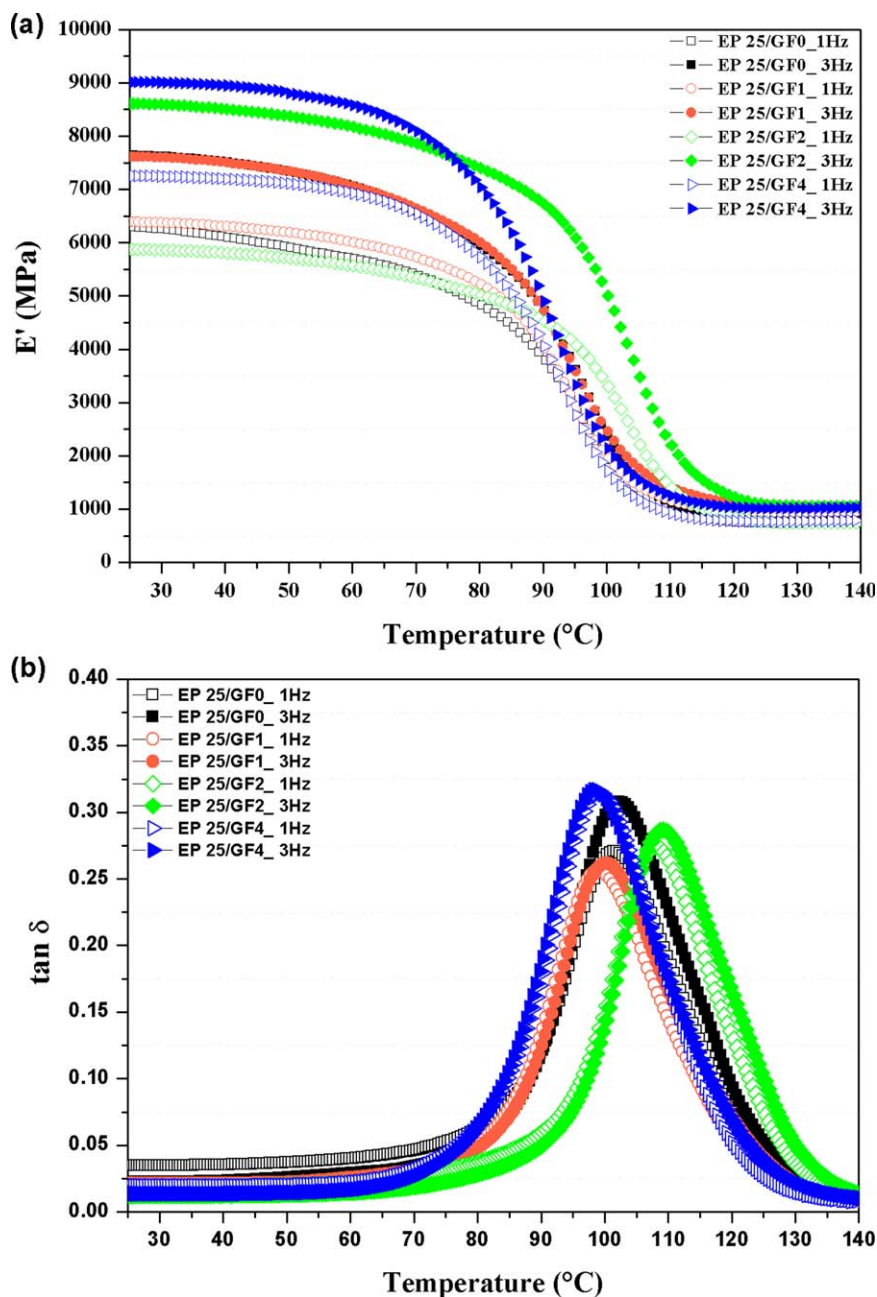


FIG. 3. E' (a) and $\tan \delta$ (b) curves of composites with 0.25% of CNT in the epoxy resin and CNT deposited on the GF fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Fig. 6. The EP0/GF0 composite was nearly transparent to the electromagnetic waves, which is basically due to the low electrical conductivity of the glass fibers (mostly composed of silica, SiO_2) [3]. The curve is quite similar to that of the aluminum plate used as reference.

However, much higher attenuation is observed for higher CNT content. As expected, the absorbing centers (i.e., the CNT) behave as a dielectric material, promoting impedance matching and facilitating propagation of the incident electromagnetic waves into the laminate. These waves are

TABLE 2. The values of E' (at 30°C) of the composites as a function of the frequency.

Composites	E' (MPa)—1 Hz	E' (MPa)—3 Hz
EP0/GF0	6274	7541
EP25/GF0	6271	7618
EP0/GF1	7562	8126
EP25/GF1	6380	7597
EP0/GF2	7223	8018
EP25/GF2	5858	8624
EP0/GF4	5064	6308
EP25/GF4	7293	8967

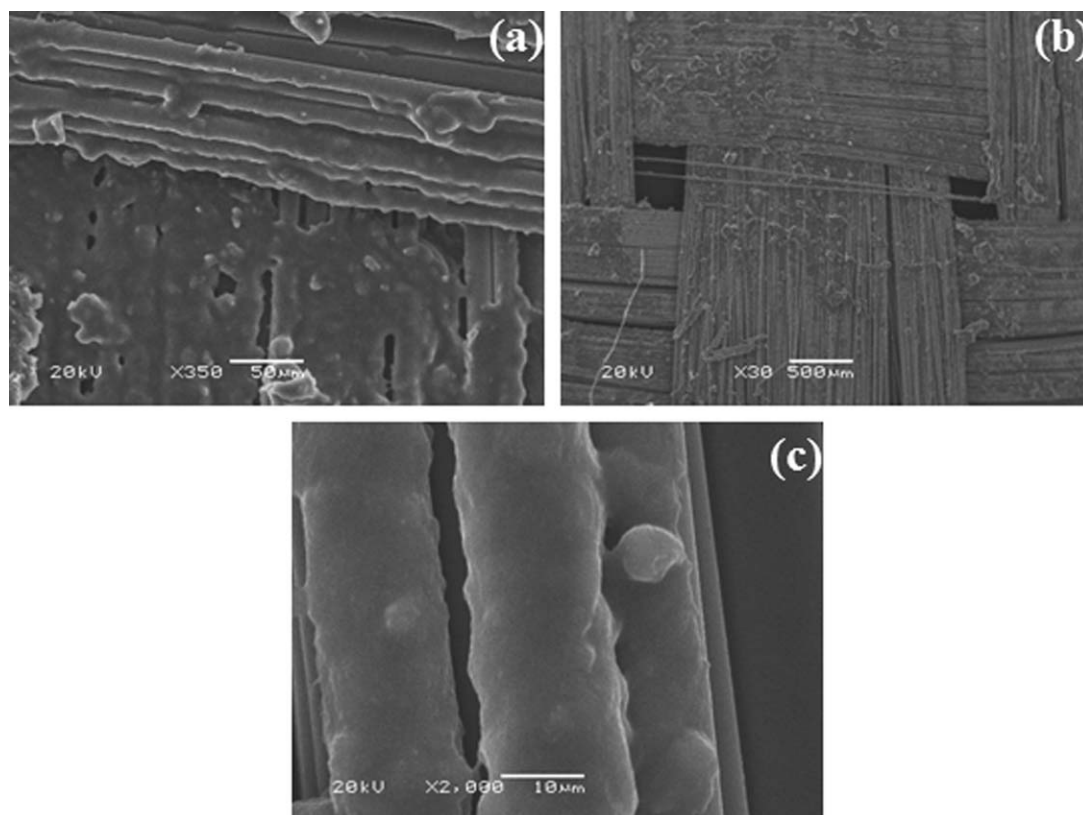


FIG. 4. SEM micrographs of the coating produced by painting (a), of the glass fiber fabric (b), and of the glass fibers after deposition of the CNT (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dissipated/absorbed depending on the amount of the absorbing center, thus increasing the loss factor [15]. The processed material can be classified as a resonant absorbing material or resonant RAM, which better operates in narrow frequency bands, as shown in Fig. 6 [16].

Maximum attenuation was achieved for the EP25/GF4 laminate, about -14 dB, which represents 96% of absorption of electromagnetic energy. The EP/GF (4% CNT) composite did not exceed that threshold probably due to imperfections in the composites originated from the manual coating and/or from the molding itself. The EP0/GF2 sample also displayed good overall performance in

attenuation of incident radiation, reaching a maximum attenuation of -12 dB (representing 94% of absorption), with a narrower attenuation frequency band, especially within 9.0–10.5 GHz. Attenuation values for the final composite produced, called EP0/GF2-WE, were higher, reaching a maximum of about 18.3 dB ($\sim 98.54\%$ of absorption), with 96% attenuation in the whole 9.9–11.1 GHz frequency range.

It may be said that if the amount of conductive filler is too small, absorption is limited because not enough dissipating elements are available to attenuate the EM wave energy. On the contrary, if too much conductivity is achieved, then the medium becomes mostly reflective. The best performance lies in the middle and has to be found for a particular resin/filler system, as this is directly associated to their intrinsic properties [13]. For the three-component composites produced, the best performance in absorption of electromagnetic waves was found for those with 2.0–2.5% of CNT.

Therefore, attenuation of electromagnetic waves may be conferred to EP/GF composites by including CNT as absorbing centers. When this material is impinged by an electromagnetic wave, the CNT induce an electrical current and the flow of the current favors wave absorption, in accordance with the modified Maxwell's law [3]. This

TABLE 3. T_g values by the $\tan \delta$ curves for all composites.

Composites	T_g by $\tan \delta$ curves at 1 Hz (30°C)	T_g by $\tan \delta$ curves at 3 Hz (30°C)
EP0/GF0	104	106
EP25/GF0	105	106
EP0/GF1	105	105
EP25/GF1	99	100
EP0/GF2	103	109
EP25/GF2	108	109
EP0/GF4	104	106
EP25/GF4	99	99

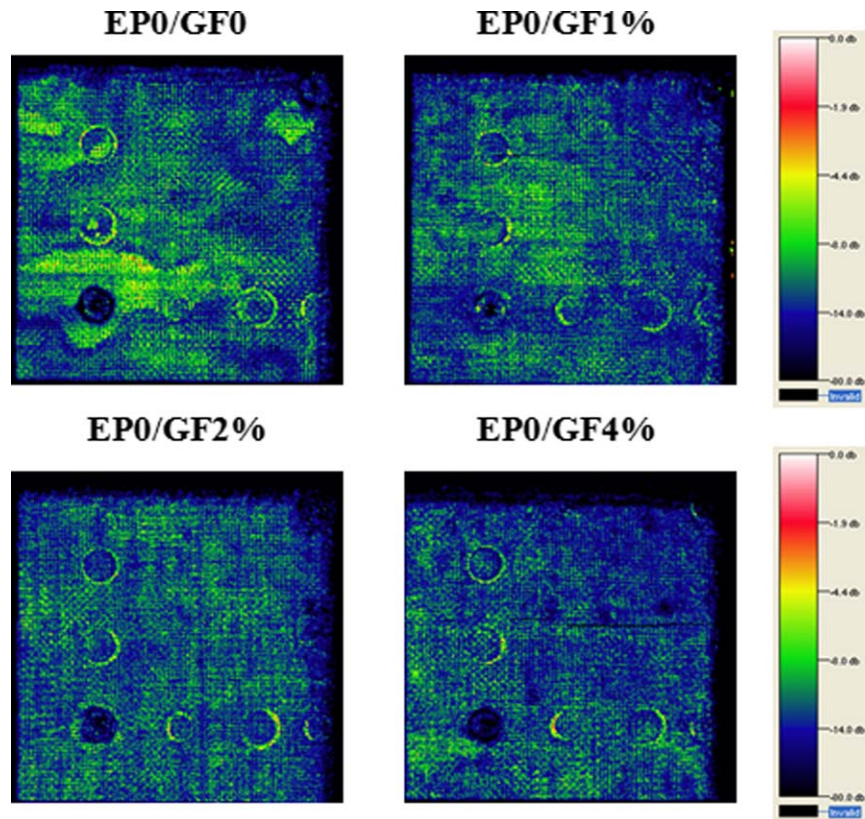


FIG. 5. C-scan images of the two-component composites produced by RTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

justifies the need for introducing high and well-distributed CNT content, and also the interest in further improving their manufacturing process.

For comparison, there are some studies in the literature focusing on the use of carbon nanotubes as absorbers cen-

ters of electromagnetic radiation. However, they use different configurations and distinct processing techniques, with variable results in terms of microwave attenuation. For example, Silva et al. [17] studied nanocomposites of carbon nanotubes dispersed in epoxy resins and reached

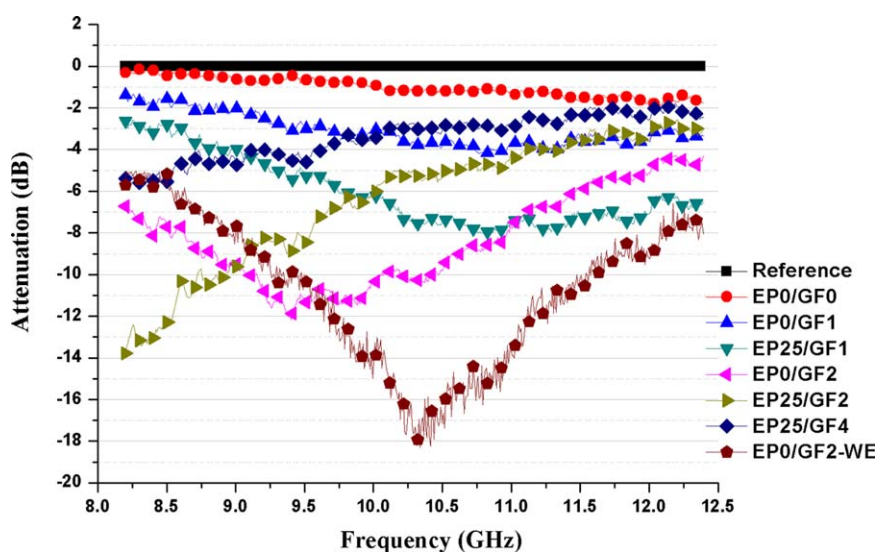


FIG. 6. Reflectivity curves as a function of frequency for two- and three-component laminates based on CNT, epoxy, and glass fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maximum attenuation of 25 dB at 11 GHz for a formulation containing 0.5 wt% of CNT, which is about 99.7% absorption, but using a 9-mm-thick composite. They also comment on the presence of carbon nanotube clusters that can act as electrical conduction islands and promote attenuation of electromagnetic wave. Folgueras et al. [18] reached only 87% of incident energy absorption (attenuation of 9.0 dB) for a composite comprised of attenuate (PPS) and glass fiber coated with a dispersion of 5 wt% of carbon nanotubes in polyurethane.

However, in this study, the tri-component composite produced by RTM consisting of epoxy resin/glass fiber coated with 2 wt% of carbon nanotubes reached 98.54% attenuation (ca. 18.3 dB), at 11.1 GHz, with 2.0 mm thick plates. It falls within the class of multifunctional composites, presenting multiple advantages, such as mechanical properties much higher than the epoxy/CNT bi-component composites. The high microwave (~98.5% at 11.1 GHz) attenuation characteristic was obtained with an absorber center (CNT) within the bulk of the composite instead of a composite surface coating, which increases its durability. Also, the RAM can be obtained by a versatile processing technique (i.e., RTM), being of low cost for the mass production of components.

CONCLUSIONS

It was possible to produce via resin transfer molding glass fiber composites with high overall CNT content (up to 4.15 wt%) following a novel, practical, low-cost, and effective method for the direct deposition of CNT onto glass-fiber fabric. An acetone/CNT/epoxy resin suspension was deposited onto the fabric, producing a type of coating on the fibers. The two-step method (deposition and molding) showed also beneficial considering that an epoxy resin filled with 0.25 wt% of CNT was used to infiltrate the fabric.

The storage modulus of the composites produced with CNT, in general, slightly increased as a function of the CNT content. A greater improvement was not noticed because the CNT was mostly located on the surface of the fibers. However, the high CNT content was of utmost importance for the development of electromagnetic characteristics on the final composite, absorbing much of the radiation in the microwave range. The microwave absorption by the composites showed an increasing trend for higher CNT content (up to 2.0 wt%), reaching a maximum of approximately -18.3 dB (98.5% of absorption). This was obtained using a comparatively low cost (glass fiber) and very thin (2.2 mm) polymer composite material. Therefore, the produced composites have shown great potential to be used as microwave-absorption materials. With further improvement in the process, these materials could become viable high performance compo-

sites for a wide range of engineering applications, from telecommunication to aerospace sectors.

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